GFS CHEMICALS®

STANDARD SUBSTANCES AND SOLUTIONS

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Published by
THE G. FREDERICK SMITH CHEMICAL COMPANY
867 McKinley Avenue
Columbus, Ohio 43223

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PREFACE

This monograph was prepared by Professor Alfred A. Schilt of Northern Illinois University with the assistance of Mr. Loren McBride, Chief Chemist of the G. Frederick Smith Chemical Company. It is intended as a ready reference for those who labor in the laboratory without easy access to extensive library materials. Comments and suggestions from interested readers as to how this monograph can be improved and made more useful will certainly be appreciated.

Chapter I. INTRODUCTION

It is a simple truth in quantitative chemical analysis that accuracy is limited ultimately by the reliability of the standards used to calibrate the instruments and/or to standardize the reagent solutions employed in the analysis. To achieve high accuracy in a given determination, once adequate precision has been attained through careful attention to instrumental and experimental details, the analyst must turn his attention to purities of chemical standards, possible interfering contaminants, and any adverse effects of storage and environment on the reliability of the chemical standards used. The importance of standards in chemical analysis merits emphasizing. Modern analytical instruments, no matter how impressive or sophisticated, still require frequent calibration with suitable standards. Titrimetric determinations, classical or modern, still depend on the use of primary standards directly or indirectly. Trouble-shooting errant analytical procedures and methods with reliable standards remains one of the most effective strategies in the analyst's approach to problem solving.

Effective use of chemical standards requires knowledge of their preparation, properties, and applications. This monograph is intended to provide such information in a single convenient source for those substances that most commonly serve as standards in chemical analysis.

Two types of standard substances, primary and secondary, are commonly recognized, although many different designations have been used to classify chemicals according to their purities. Any chemical substance that is classified as a primary standard should ideally possess the following desirable characteristics: readily prepared and dried to a known definite composition; a purity of the order of 99.9-100.1% or better, verifiable by assay; the absence of potentially interfering impurities as demonstrated by easily applied and sensitive qualitative tests; sufficient stability to withstand any permanent change in composition during storage under ordinary conditions; not hygroscopic so that it can be weighed reliably in air; and a relatively high equivalent weight so as to minimize relative error in weighing samples taken for standardization purposes. Strict requirements such as these greatly limit the number of reagent chemicals that qualify as primary standard substances. Even some generally acceptable primary standards do not satisfy all of the ideal requirements, especially with regard to high stability and equivalent weight. Not surprisingly, the lack of an adequate variety of primary standards has given rise to the need for secondary standards. These are reagent quality substances that have been carefully tested and analyzed to assure accurately known but not necessarily absolute purity. Frequently, their purity is based upon a primary standard which was employed to standardize the titrimetric solutions used to assay purity; thus they are secondary standards. The major distinctions then between primary and secondary standards is that the former can be readily prepared in high purity (99.9+%) and need only be qualitatively tested (not assayed) to make certain that interfering contaminants are absent or negligible, whereas the latter always requires accurate determination (assay) of the major ingredient.

A standard solution is prepared in known concentration by dissolving an accurately weighed amount of a primary standard in a suitable solvent and diluting to a known volume. For highest accuracy the temperature should be controlled so as to control volume and hence concentration reproducibly. If the temperature is to be allowed to vary, the standard solution is best prepared by mixing known weights of both the solute and the solvent, since concentration by mass is temperature independent. If a suitable primary standard is not available to prepare the standard solution directly, the solution is prepared with either a secondary standard or a reagent quality substance, and then standardized against a primary standard. For highest accuracy a primary standard rather than a secondary one is advisable.

Brief mention is appropriate here regarding other grades of chemicals. Commercial or technical grade substances are commonly impure, useful industrially, but not considered suitable for laboratory reagent use. U.S.P. grade chemicals are purified to pass specifications set by the current U.S. Pharmacopeia; these are usually suitable for ordinary laboratory use, although less pure than reagent grade chemicals. Reagent grade chemicals are highly purified, suitable for quantitative analytical applications, and commonly carry the manufacturer's control analysis on their labels. Certain reagent grade chemicals are designated "Meets A.C.S. Specifications", meaning that they satisfy the requirements set forth in the latest edition of "Reagent Chemicals, American Chemical Society Specifications" (1). These substances are ideally suited for all analytical purposes except possibly as standards. Various suppliers and chemical manufacturers employ their own special designations for grades and purities, but these fall by and large under one of the above categories.

Finally, a note of caution is in order, along with some recommendations concerning verifying the purity of reagents. As Kolthoff and others have correctly pointed out (2), the statement of analysis on a reagent bottle may not always be correct for various reasons, so when in doubt one should test the reagent for impurities that may interfere in the intended determination. If the purest reagent obtainable is too impure it must be purified by an appropriate method. In the case of a primary standard substance, it is best to guard against possible contamination at all times and when in doubt repeat the appropriate purification step prior to use.

Chapter II. STANDARDS FOR ACID-BASE TITRATIONS

Primary Standard Acids

Numerous acids have been proposed but relatively few qualify as ideal primary standard substances. These are most commonly used to standardize solutions of sodium hydroxide and other strong bases. Rarely are they suitable for titrating weak bases, because they are considerably weaker than the mineral acids commonly employed for this purpose. Probably the most frequently used acidimetric standard is potassium hydrogen phthalate. Constant boiling hydrochloric and perchloric acids have been recommended as primary standards, but these solutions do not meet all of the ideal requirements of a primary standard. They are included here with other commonly used standard acids because they are strongly acidic and can be used to prepare standard solutions by accurate dilution. Weak as well as strong bases can be titrated with these.

Potassium Hydrogen Phthalate

(Potassium acid phthalate, Potassium biphthalate, Phthalic acid monopotassium salt, KHP)
$HOCOC_6H_4COOK$ F.W. 204.23 (E.W. = 204.23 as monoprotic acid)

This commonly used acidimetric standard is best prepared according to Hendrixson (3) by treating a solution of pure sublimed phthalic anhydride with a slight excess of the theoretical quantity of anhydrous potassium carbonate to half-neutralize the phthalic acid and crystallizing three times from water. It has a water solubility of 12.7% at 35 °C and 36.1% at 100 °C. The purified product can be dried at 125 °C, but at higher temperatures decomposition occurs attended by sublimation of phthalic anhydride.

Current specifications for primary standard grade KHP as set by the American Chemical Society (1) are as follows: assay, 99.95-100.05% $C_8H_5O_4K$; insolubles, 0.005% max.; pH of 0.05 $\underline{M}$ solution, 4.00 at 25 °C; chlorine compounds (as Cl), to pass test (limit about 0.003%); sulfur compounds (as S), to pass test (limit about 0.002%); heavy metals (as Pb), not more than 0.0005%; iron (Fe), not more than 0.0005%; and sodium (Na), not more than 0.005%.

Primary standard grade KHP is commercially available, GFS catalog No. 554. Its purity can be checked, if necessary, by the assay procedure recommended by the ACS which involves comparison of the sample with a National Bureau of Standards certified sample of potassium hydrogen phthalate. Accurately weighed samples of the two are each treated with accurately weighed portions of anhydrous sodium carbonate, dissolved in water, and the excess acid in each is titrated (after purging and boiling the solution to remove carbon dioxide) with carbonate-free sodium hydroxide to a phenolphthalein end-point. Other methods can be used to verify assay but the ACS method is normally prescribed. A quick test consists of titrating two accurately weighed samples (0.8-0.9 g), one the KHP sample and the other a NBS standard KHP sample, with the same 0.1 $\underline{M}$ NaOH titrant, both to a pH 8.5 end-point.

Potassium hydrogen phthalate can be used as a standard to calibrate pH meters as well as to standardize solutions of strong bases. Before such uses it should be crushed (not ground) in an agate or mullite mortar to approximately 100-mesh fineness, dried for 2 hours at 120 °C, and cooled in a desiccator. To standardize 0.1 M alkali, dissolve an accurately weighed sample (0.8 g) of the KHP (dried as above) in 75 ml of warm water (CO_2-free) and titrate with the alkali solution using phenolphthalein as indicator. To prepare a pH 4.00 (at 25 °C) buffer solution for use in calibrating pH meters, dissolve 1.02 g of the dried material in 100 ml of distilled (CO_2-free) water.

Benzoic Acid

C_6H_5COOH F.W. 122.12 (E.W. = 122.12)

Except for its limited solubility in water (2.9 g/l at 20 °C, 4.2 g/l at 30 °C and 6.0 g/l at 50 °C), benzoic acid is an excellent primary standard for standardizing strongly basic titrants. Ethanol or methanol is sometimes added to increase its solubility for titrations involving aqueous solutions. Solubility is much less a problem in certain nonaqueous solvents, so benzoic acid finds frequent application as a standard in nonaqueous titrimetry. It also serves as a standard in calorimetry.

Preparation of ultra-pure benzoic acid had been described by Swab and Wichers (4). A certified standard sample of 99.98% purity is available from the National Bureau of Standards. Reagent grade benzoic acid may be purified by crystallizing it twice from ethanol, once from water, and subliming the crystallized product in vacuum. The fluffy sublimed product can be melted in a platinum vessel at 125-130 °C to obtain a fused material which is easier to handle. It is not hygroscopic and is easily freed of superficial moisture by drying at 100 °C.

To standardize 0.1 M alkali, dissolve an accurately weighed sample (0.5 g) of the benzoic acid (dried at 100 °C for one hour) in 20 ml of neutral ethanol (CO_2-free) and titrate with the aqueous alkali solution to be standardized using phenolphtalein as indicator. Also titrate a blank to correct for the titrant consumed by the solvent and indicator.

Sulfamic Acid

(Amidosulfonic acid)
NH_2SO_2OH F.W. 97.10 (E.W. = 97.10 as monoprotic acid)

The advantages of sulfamic acid as an acidimetric standard, as reviewed by Butler, Smith, and Audrieth (5), include ease of purification, ready solubility, and high strength as a monoprotic acid which enables very precise end-point detection and a broad choice of suitable indicators. Its low equivalent weight and the difficulty of removing trace amounts of occluded water exclude it from the list of ideal primary standards. Nevertheless, because of the ease of preparing samples with purities consistently of the order of 99.95%, sulfamic acid qualifies as an excellent working standard for acidimetry. GFS lists two primary standard grades, catalog nos. 97 and 98.

Sulfamic acid melts with decomposition at 205 °C, preventing use of fusion to remove occluded water (estimated to be of the order of 0.05%). Superficial moisture can be readily removed by exposure to dry air at room temperature, and the product is non-hygroscopic. In aqueous solution sulfamic acid undergoes slow hydrolysis to form ammonium hydrogen sulfate, which is a strong monequivalent acid like sulfamic acid so that fortunately the number of equivalents of strong acid remains unchanged and no change in normality is detectable.

Commonly prepared by reactions of chlorosulfonic acid with ammonia, or by heating urea with sulfuric acid, sulfamic acid can be purified by crystallizing from water (soluble in 6.5 parts of water at 0 °C and in 2 parts water at 80 °C). A 1% solution has a pH of 1.18 at 25 °C.

Prior to use as an acidimetric standard the sulfamic acid should be ground and dried by long storage over anhydrous magnesium perchlorate or in an oven at 100 °C for one hour. To standardize 0.1 M alkali, dissolve an accurately weighed sample (0.4 g) of the dry sulfamic acid in 50 ml of water and titrate with the alkali solution using any indicator showing color change between pH 4.5 to 9 (for example; bromothymol blue, methyl orange, or phenolphthalein).

Potassium Hydrogen Iodate

(Potassium acid iodate, Potassium bi-iodate)
$KH(IO_3)_2$ F.W. 389.94 (E.W. = 389.94 as a monoprotic acid)

Useful as a primary standard for both acidimetry and oxidimetry (iodimetry) this substance is strongly acidic so that sharp end-points are obtained with either methyl yellow or phenolphthalein indicator in titrations with strong bases. It is not hygroscopic, stable both in solution and as a solid, easy to prepare, and simple to purify by crystallizing from water.

Pure potassium acid iodate can be prepared (6) by treating a solution of potassium iodate in boiling water with an acidified (HCl) solution of iodic acid, cooling to obtain the crystallized product, and crystallizing from water three more times. The crystals may be dried at 120 °C but no higher. Assays of purity typically give values between 99.97 and 100.03%. Two GFS primary standard grades are available.

To standardize 0.1 M alkali, dissolve an accurately weighed sample (1.5 g) of $KH(IO_3)_2$ (dried at 100 °C for two hours) in 50 ml of water (CO_2-free) and titrate with the alkali solution using either methyl yellow or phenolphthalein indicator.

Constant-Boiling Hydrochloric Acid

When an aqueous solution of hydrochloric acid is boiled at a given atmospheric pressure its composition changes until a point is reached when the composition of the vapor and that of the liquid become identical. At this point, both the boiling point temperature and the composition of the solution remain constant, regardless of further boiling, so long as the barometric pressure remains unchanged. Such a solution (azeotrope) has a well-defined, precise, and easily reproducible composition (dependent only on the atmospheric pressure) that is suitable for standardization purposes. Hulett and Bonner (7) were first to recommend constant-boiling hydrochloric acid for the preparation of standard solutions. The concentrations of the constant-boiling mixtures as a function of atmospheric pressures during distillation are listed in Table 1. (8) (9) These data are accurately calculated to within one part per thousand, according to King (10), using the following empirical equation:

$$G = \frac{P + 7680}{46.8386}$$

where G is the air weight in grams required to contain exactly one mole of HCl, and P is the corrected barometric pressure in mm Hg at which the constant boiling acid was collected.

Constant-boiling hydrochloric acid is commonly prepared starting with one liter of hydrochloric acid of sp. gr. 1.18 which is distilled at a rate of 3-4 ml/min. After 750 ml of the original volume has been distilled, the constant-boiling fraction is collected until a residue of not less than 50-60 ml remains. The barometer is read to within 1 mm and the composition is deduced from Table 1 or the empirical equation of King. If the distillation is carried out at 760 mm, then 18.019 g of the constant-boiling acid is diluted to exactly one liter to prepare 0.1000 M hydrochloric acid.

Table 1. Composition of Constant-Boiling Hydrochloric Acid

Barometric Pressure (mm Hg)	% HCl (by weight in vacuo)	Grams/mole HCl (in air vs. brass weights)
600	20.638	176.55
640	20.507	177.68
680	20.413	178.50
700	20.360	178.96
730	20.293	179.55
740	20.269	179.77
750	20.245	179.98
760	20.221	180.19
770	20.197	180.41
780	20.173	180.62

Constant-Boiling Perchloric Acid

Smith and Koch (11) recommended the use of constant-boiling perchloric acid as a standard for acidimetry. Their procedure for preparing standard 73.60% perchloric acid (corresponding to the dihydrate $HClO_4 \cdot 2H_2O$) by vacuum distillation is summarized in the following paragraph.

Pure 72% perchloric acid is distilled under a vacuum of 2-7 mm in an appropriate apparatus. When one-half of the acid has distilled over, a clean dry receiver is used to collect the second fraction distilled under the same conditions. The rate of distillation is not critical; and the distillate collected at this stage, even if the temperature varies between 60 and 95 °C, has an acid content of 73.60 ± 0.03 percent by weight perchloric acid. If 71 % perchloric acid is used as starting material, the procedure is the same except that the first 60% of the distillate is discarded; and for 70% acid, the first 65% of the distillate is discarded. The constant-boiling acid is slightly hygroscopic and fumes faintly so that appropriate precautions should be taken in storing and weighing it. Proper safety precautions should also be observed because of the risk of fire or explosion when concentrated perchloric acid is contacted with oxidizable material, especially at high temperatures. (12)

To prepare a 0.1000 M solution of $HClO_4$ a 13.642-g sample of the above preparation is diluted to exactly one liter with distilled water. The GFS product no. 65 offers this acid in 10-ml ampules with exact weight given.

Other Standard Acids

Many other organic acids and acidic salts have been recommended as primary standards but for one reason or another have not proven widely accepted. Some of these are described briefly below and more fully in reference (6). For a list of most of the others, reference (13) may be consulted.

Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) has the disadvantage that it is difficult to obtain a product entirely free from salts and with exactly two moles of water per mole of acid. Also, the second ionization constant of oxalic acid is relatively small so that end-point detection (corresponding to the second equivalence point) is less precise than that for stronger acids.

Potassium tetroxalate ($KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$) requires hygrostatic control to attain a definite hydrate composition.

Potassium acid oxalate (KHC_2O_4) can be crystallized without water of hydration but occluded water is a problem.

Potassium bitartrate ($KHC_4H_4O_6$) is only slightly soluble in cold water but suitably soluble for use if warm solutions are titrated.

Primary Standard Bases

Several popular choices of alkalimetric standards are available for standardizing dilute solutions of strong acids: sodium carbonate, borax, and tris(hydroxymethyl)aminomethane. Primary standard grade samples of these are readily available. These and several other alkalimetric standards are briefly described below.

Sodium Carbonate

Na_2CO_3 F.W. 105.99 (E.W. = 53.00 or 105.99, depending on use)

First recommended as a primary standard in 1897 by Lunge (14), sodium carbonate is a much used alkalimetric standard. It is most conveniently prepared by heating reagent grade sodium carbonate at 260-

285 °C in an electric furnace with occasional stirring for two hours. This assures that all moisture is removed and any sodium bicarbonate is decomposed with loss of water and carbon dioxide to form sodium carbonate. After cooling in a desiccator the product should be protected from undue exposure to the atmosphere to prevent absorption of water and carbon dioxide and formation of sodium bicarbonate by the following reaction:

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

An alternate method starts with reagent grade sodium bicarbonate which is added with stirring to water heated at 80 °C until the solution is saturated (carbon dioxide is evolved during this stage). After the hot solution is filtered and cooled to 10-15 °C, the coarsely crystalline salt $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ precipitates. This material, after collection, washing and air-drying can be heated at 260-285 °C as described above to obtain pure sodium carbonate.

Specifications for alkalimetric standard sodium carbonate as set by the American Chemical Society are as follows: assay, 99.95-100.05% Na_2CO_3; insolubles, 0.010% max.; loss on heating at 285 °C, 1.0% max.; chloride (Cl), 0.002% max.; nitrogen compounds (as N), 0.001% max.; phosphate (PO_4), 0.001% max.; silica (SiO_2), 0.005% max.; sulfur compounds (as SO_4), 0.003% max.; ammonium hydroxide precipitate, 0.010% max.; arsenic (As), 0.0001% max.; calcium and magnesium precipitate, 0.010% max.; heavy metals (as Pb), 0.0005% max.; iron (Fe), 0.0005% max.; and potassium (K), 0.005% max.

To verify the assay of primary standard grade sodium carbonate an accurately measured sample of dry N.B.S. certified potassium hydrogen phthalate is treated with an accurately measured quantity of the sodium carbonate to be tested. The KHP should be taken so as to be in slight excess of the sodium carbonate. After purging and boiling the solution to remove carbon dioxide, the slight excess of KHP is determined by titration with 0.020 $\underline{M}$ sodium hydroxide using phenolphthalein as the indicator. Further details of this assay procedure can be found in reference (1).

Sodium carbonate tends to absorb moisture so that an error of 0.1% due to an increase in weight may easily arise in weighing out the small quantity needed for standardizing 0.1 $\underline{M}$ acid. A covered crucible or weighing bottle therefore should be used in weighing the standard in order to minimize moisture absorption.

To standardize 0.1 $\underline{M}$ strong acid, dissolve an accurately weighed sample (0.22 g) (weighed in a covered weighing bottle) of sodium carbonate (dried at 285 °C as described above) in 25 ml of water, add a few drops of bromocresol green indicator, and titrate with the acid solution to be standardized until the color changes from blue to green; then heat the solution to boiling until the color changes back to blue; finally, cool the solution to room temperature, and complete the titration by titrating to the point at which the color changes once again from blue to green.

Borax

(Sodium borate, Sodium tetraborate decahydrate)
$Na_2B_4O_7 \cdot 10H_2O$ F.W. 381.37 (E.W. 190.68)

Recommended by many as a primary standard (15), borax has only two relatively minor disadvantages: it is difficult to test thoroughly for impurities, and it is best "dried" in a hygrostat at 70% relative humidity to assure a definite decahydrate composition.

In dry air, crystals of borax effloresce (disintegrate into a white powder) on losing water to form the pentahydrate. Exposed to moist air, borax can absorb carbon dioxide and become contaminated with carbonate or bicarbonate. Such contamination is difficult to detect except by gravimetric determination of the carbon dioxide liberated by acidification. Thus, borax is best stored in a tightly closed container or in a hygrostat. A convenient hygrostat to maintain a relative humidity of 70% is a desiccator containing a solution saturated with respect to both sucrose and sodium chloride in contact with an excess of each solid.

In addition to its use as an alkalimetric standard, borax can be used in solution as a pH standard to calibrate pH meters and buffers. A 0.01 $\underline{M}$ solution of NBS certified borax has a pH of 9.180 at 25 °C. Ordinary reagent-grade borax, according to ACS specifications, in a 0.01 $\underline{M}$ solution, should have a pH between 9.15 and 9.20 at 25 °C; such a solution can thus serve as a convenient approximate standard for pH measurement.

For use as a primary standard, reagent-grade borax should be crystallized twice from water at temperatures below 55 °C (to assure formation of the decahydrate). Its solubility is 3 g per 100 ml at 25 °C and 30 g per 100 ml at 55 °C. After washing first with water, then 95% ethanol, and finally diethyl ether, the crystals should be sucked dry to remove traces of the ether and stored in a desiccator over saturated $NaBr \cdot 2H_2O$ or saturated sodium chloride-sucrose solution.

To standardize a 0.1 $\underline{M}$ solution of strong acid, dissolve an accurately weighed (0.76 g) sample of borax ("dried" in 70% relative humidity as described above) in 50 ml of water and titrate with the acid solution to be standardized using methyl red as indicator. The equivalence point can be attained to within ± 0.01 ml if a solution of boric acid, sodium chloride and indicator, corresponding to that of the equivalence point in the titration, is used as a color reference for purpose of matching.

Tris(hydroxymethyl)aminomethane

(THAM, "TRIS")
$(CH_2OH)_3CNH_2$ F.W. 121.14 (E.W. = 121.14 as a base)

Unlike either borax or sodium carbonate, THAM and its solutions do not absorb carbon dioxide from the air and thus are simpler to use and freer from risk of atmospheric contamination. Except for the minor disadvantages that it cannot be heated above 100 °C indiscriminately and it is not as strong a base as other available alkalimetric standards, tris(hydroxymethyl)aminomethane fulfills all the requirements of a good primary standard (16).

Tris(hydroxymethyl)aminomethane is commercially available in high purity, GFS nos. 176 and 375. Technical grade material can be purified by crystallization three times from hot (50-60 °C) water by adding methanol and cooling to 3-4 °C. Details are given in reference (16). Drying is facilitated by grinding the air-dried product to pass a 50-mesh screen. Any of several different methods can then be used to dry THAM to a definite composition free of moisture. It can be dried in a vacuum oven for 12 hours at 60 °C at a pressure of not more than 10 to 15 mm, or in a vacuum desiccator over anhydrous magnesium perchlorate, or in an oven for 2 to 4 hours at 100-103 °C. Decomposition with a detectable loss (1%) in weight results on heating THAM at 110 °C for 10 hours (16).

In addition to its use as an alkalimetric standard, THAM is frequently employed as a component to prepare buffer solutions of pH 7 to 9. Such buffers are often referred to collectively as "tris-buffer". The NBS provides standard reference materials for preparation of a tris-buffer of pH 7.699 at 25 °C for standardizing pH meters.

To standardize 0.1 M strong acid, dissolve an accurately weighed sample (0.48 g) of tris(hydroxymethyl)aminomethane (dried as described above) in 50 ml of water and titrate with the acid solution using either p-sulfo-o-methoxybenzeneazodimethyl-1-naphthylamine or potentiometric end-point detection. The pH at the equivalence point (marked by a sharp and well-defined break) is approximately 4.7. Other suitable indicators include ethyl orange and a mixed one consisting of equal parts of 0.1% solutions of bromocresol green and sodium alizarin sulfonate.

Other Alkalimetric Standards

Potassium iodate (17) (GFS no. 79), mercuric oxide (18), diphenylguanidine (19) (GFS no. 136) and 4-aminopyridine (20), among others, have been recommended for use in standardizing solutions of strong acids. Potassium iodate also finds application for standardizing thiosulfate solutions, and mercuric oxide for thiocyanate solutions.

When potassium iodate is employed it is necessary to add potassium iodide and excess sodium thiosulfate to the solution of the weighed sample of KIO_3 before titrating to a methyl red end-point with the acid solution to be standardized. Because the iodine (liberated from the reaction of iodate with iodide and hydrogen ion) is reduced by the thiosulfate, the net titration reaction is as follows:

$$IO_3^- + 6H^+ + 6S_2O_3^= \rightarrow 3S_4O_6^= + I^- + 3\,H_2O$$

A slight excess of the titrant at the end point imparts acidity to the solution and converts the color of methyl red from yellow to red.

Use of mercuric oxide is probably best avoided because of health hazards and environmental protection concerns. Primary standard 4-aminopyridine has the advantage over diphenylguanidine because of its greater water solubility.

Standard Solutions

Some general comments, applicable to all standard titrants, are appropriate before focusing on specific standard solutions or titrants. In preparing a standard solution it is generally preferable and more convenient to prepare it directly by dissolving the accurately weighed primary standard grade substance and diluting it to a known volume in a volumetric flask. If a suitable standard substance is unavailable, the solution is prepared to have the approximate desired concentration and then standardized against a primary standard. To compensate for certain titrimetric errors the solution should be standardized with the same substance, volumetric ware, and experimental conditions (especially temperature) as will pertain to its eventual use. Relative error is always minimized by taking samples for titration of optimum size such that the volume of titrant required will be no more and only slightly less than that contained by the buret used - e.g., 40 ml for a 50-ml buret. For high accuracy the indicator blank should be determined and subtracted from the total titration volume, although for general purposes this correction is usually small and frequently neglected. Standard solutions should always be stored in tightly-closed containers and, because of evaporation and condensation upon the inner surfaces of the container, always shaken well before withdrawing any portion. Unused portions should never be returned to the storage container.

The effect of temperature on solution volumes, and hence on molarity or normality, should not be ignored if accurate results are desired. Ideally, whenever standard solutions are to be standardized or measured from pipets or burets their temperature should be brought to and held at 20 °C to within ± 1 °C if the relative error is to be no more than 0.2-0.3 ppt, or to ± 5 °C if no more than 2 ppt relative error can be tolerated. For convenience, instead of adjusting the temperature it can be measured and a temperature correction applied (see Table A-1 in the appendix).

Details of the preparation, standardization, and storage of some of the more commonly used titrants for acid-base titrimetry in aqueous as well as nonaqueous solvents are summarized in the following subsections.

Hydrochloric acid (aqueous)

Standard solutions of the desired concentrations can be prepared directly by accurate dilution of constant boiling acid, as described above, and require no standardization. Otherwise, approximate solutions can be prepared by diluting the calculated amount of concentrated reagent grade hydrochloric acid (see Tables A-2 and A-3 in Appendix) and standardized with one of the primary standard bases described above. To prepare one liter of 0.1 M HCl, dilute 8.3 ml of concentrated hydrochloric acid (37.2%, 1.19 sp. gr., 12.1 M) to a volume of one liter with distilled water. Transfer the solution to a glass-stoppered bottle, standardize, and label. If protected against contamination and loss by evaporation, standard hydrochloric acid solutions can be stored indefinitely without change in molarity.

Perchloric acid (aqueous)

Constant boiling perchloric acid, described above, can be accurately measured and diluted to prepare standard solutions directly. For example, to prepare exactly 1 M $HClO_4$ dilute 136.45 g of the 73.60% $HClO_4$ to exactly one liter with distilled water. Other perchloric acid compositions of known densities can be employed by diluting the calculated amount (see Tables A-2 and A-3 in Appendix) to the correct volume with distilled water. To prepare 0.1 M $HClO_4$ from 70% perchloric acid (1.67 sp. gr., 11.7 M), for example, dilute 8.6 ml of the concentrated acid to one liter with distilled water. After standardization with a primary standard base the standard perchloric acid solution can be stored indefinitely without change in glass-stoppered glass containers.

Sodium hydroxide (aqueous)

Reagent grade sodium hydroxide commonly contains small amounts of silicate, chloride and sulfate as well as appreciable amounts of water and carbonate. This is true also of the other alkali and alkaline earth hydroxides, so that a primary standard grade metal hydroxide is unavailable. A reliable standard solution is therefore prepared in a particular way so as to be essentially freed of carbonate, carefully protected against subsequent exposure to atmospheric carbon dioxide, and accurately standardized just before use. It is important that the solution be and remain carbonate-free, otherwise its effective normality will depend upon the choice of indicator and whether or not the carbonate impurity is neutralized to bicarbonate or carbon dioxide ("carbonic acid").

Of the various methods for preparing carbonate-free solutions of sodium hydroxide, perhaps the most convenient and effective procedure is that which takes advantage of the very low solubility of sodium carbonate in concentrated sodium hydroxide solution. Pure sodium hydroxide (50 g) is dissolved in an equal weight of water (50 ml) by shaking in a polyethylene bottle (tightly sealed with a screwcap). After standing for several hours (or overnight) the bottle and contents are centrifuged to obtain a clear carbonate-free supernatant that can be decanted from the denser insoluble sodium carbonate layer as needed. This solution then serves as the stock solution for preparing less concentrated solutions.

To prepare a 0.1 M solution of carbonate-free sodium hydroxide, 4 ml of the concentrated stock solution is decanted from the polyethylene bottle, transfered into another polyethylene bottle and diluted to approximately one liter with carbon dioxide-free water. A convenient source of CO_2-free water is that from a mixed-bed deionizer. Another is distilled water which has been purged with nitrogen until the pH is 5.7 or greater. Water which is suitably free of carbon dioxide will not require more than 0.1 ml of 0.1 M sodium hydroxide to give a phenolphthalein end-point when a 500-ml portion is titrated.

Once prepared and standardized against one of the primary standard acids described in this Chapter, the sodium hydroxide should be stored in a tightly closed polyethylene bottle. Brief exposure to atmospheric carbon dioxide, for example during transfer to a buret, does not give rise to any appreciable carbonate uptake; however, it is recommended that an automatic buret be used and connected with the stock bottle in such a way that contamination is eliminated. Both buret and stock bottle should be fitted with soda-lime tubes for protection against atmospheric carbon dioxide. Suitable titration assemblies are common and available commercially.

Perchloric acid (nonaqueous)

For nonaqueous titration of weak bases, a 0.1 M solution of perchloric acid in an appropriate nonaqueous solvent is the most commonly used titrant (21). Sulfuric or hydrochloric acid are not recommended because neither is as strong as perchloric acid, hydrochloric acid tends to be too volatile in nonaqueous solvents, and sulfuric acid's diprotic behavior gives rise to poorer (less sharp) end-points.

A 0.1 M solution of perchloric acid in the nonaqueous solvent of choice (commonly glacial acetic acid, dioxane, or acetic anhydride) is prepared by mixing 8.5 ml of 72% perchloric acid with 200-300 ml of glacial acetic acid (or other solvent of choice) followed by addition of 20 ml of acetic anhydride (if a completely anhydrous solution is desired) and sufficient additional solvent to make the total volume one liter. The reaction between the water from the aqueous perchloric acid and the added acetic anhydride is essentially complete after a few hours at room temperature or ten minutes if heated just below boiling. To standardize the solution dissolve an accurately weighed sample (0.5 g) of dry potassium acid phthalate in 60 ml of acetic acid (reflux gently for a few minutes to hasten dissolution) and titrate with the 0.1 M perchloric acid solution using a few drops of methyl violet (0.2 g in 100 ml of chlorobenzene) as the indicator, which at the end-point changes from violet to blue. It should be noted that the KHP in this application serves as a primary standard base (rather than an acid as in aqueous titrations). It is neutralized to phthalic acid, hence its equivalent weight is 204.23, the same as its formula weight.

Tetra-n-butylammonium hydroxide (nonaqueous)

For nonaqueous titration of weak acids, a 0.1 M solution of tetra-n-butylammonium hydroxide in 2-propanol or a mixture of benzene and methanol is the most widely used titrant (21). It has two major advantages over alkali metal alkoxide titrants: it forms salts with acids that tend to be much more soluble in nonaqueous solvents than the corresponding alkali metal salts and excellent potentiometric titration curves can be obtained using ordinary glass and calomel electrodes.

It is difficult to prepare the titrant free of such impurities as tertiarybutylamine and carbonates that cause poorly defined indicator end-points or multiple inflection-points in potentiometric titration curves. The preparation procedure of Marple and Fritz (22) provides the purest form, a crystalline hydrate that can be stored in the refrigerator for extended periods without decomposition and dissolved in 2-propanol as needed to prepare the titrant. Preparation is also practical by passing a solution of tetrabutylammonium iodide through an anion-exchange column with the resin in the hydroxide ion form (23).

A convenient way to prepare the titrant is to use commercially available 25% tetrabutylammonium hydroxide in methanol. Dilution of 100 g of this solution to one liter with 2-propanol gives a solution that is approximately 0.1 M. It should be protected from carbon dioxide by storing it in either an automatic buret or a stoppered bottle under nitrogen. To standardize, titrate an accurately weighed 75-mg sample of benzoic acid dissolved in 25 ml of 2-propanol using three drops of thymol blue indicator (0.3 g in 100 ml of 2-propanol). Use of an automatic buret and a nitrogen atmosphere (to exclude CO_2) is recommended. The end-point is taken as the first permanent blue color, and a blank titration is advisable to correct for the amount of titrant consumed by any acid impurities in the solvent or absorbed from the surroundings during the titration.

Chapter III. STANDARDS FOR REDOX TITRATIONS

Standard solutions of oxidants and reductants are prepared either by accurately weighing the primary standard grade material and diluting to a known volume or by preparing the desired approximate concentration and standardizing with a suitable primary standard. The most commonly used primary standards for these purposes are described below. The choice of which primary standard to employ for a given standardization is often based on what substance it is that will be determined by titration with the titrant. Compensation of related errors, those that depend on the nature of the reactants and the titration, can be achieved if the same substance is employed for the standardization as that which is to be subsequently determined by titration.

Primary Standard Oxidants

Potassium Dichromate

(Potassium bichromate)
$K_2Cr_2O_7$ F.W. 294.18 (E.W. 49.03, based on reduction to Cr(III))

Primary standard grade potassium dichromate can be prepared by crystallizing the reagent grade material three times from water. The bright orange-red crystals can be dried at 200 °C and stored indefinitely without decomposition. The product is not hygroscopic. It is soluble in water to the extent that a saturated solution contains 50.2% by weight $K_2Cr_2O_7$ at 100 °C, 31.3% at 60 °C, 11.7% at 20 °C and 4.3% at 0 °C. A 1% solution in water has a pH of 4.04, a 10% solution a pH of 3.57. Certified samples with assays between 99.97 and 100.03% are available commercially (GFS no. 78) and from the National Bureau of Standards.

As a primary standard, potassium dichromate is used to standardize solutions of such reductants as iron(II), tin(II), hydroquinone, tellurium(IV) and tungsten(III). It has been used as a titrant for the direct determination of these same substances and for the indirect determination of iron(III), cobalt(III), nitrate, chlorate, and peroxides, among others. It is frequently employed as a primary standard for sodium thiosulfate solutions, taking advantage of its stoichiometric and quantitative reaction in acid solution with iodide to generate an exact amount of iodine which can then be titrated with the thiosulfate solution.

To prepare one liter of 0.1000 N $K_2Cr_2O_7$, dissolve 4.903 g of the primary standard grade substance (dried for one hour at 110 °C) and dilute to exactly one liter with distilled water. This solution can be stored indefinitely without need of standardization so long as no loss by evaporation occurs.

Ceric Ammonium Nitrate

(Cerium(IV) ammonium nitrate, Ammonium hexanitratocerate(IV))
$(NH_4)_2Ce(NO_3)_6$ F.W. 548.26 (E.W. = 548.26)

A reasonably pure product (99.5%) can be prepared by dissolving thorium-free ceric oxide in hot, concentrated nitric acid followed by addition of an equal volume of water and the theoretical amount of ammonium nitrate, and concentrating by heating to cause precipitation. The orange crystals can be purified further by crystallizing again from concentrated nitric acid in the presence of ammonium nitrate. Drying to constant weight at 85 °C provides an anhydrous product of purity within the 99.95-100.03% range (24). Primary standard as well as certified purity grade samples are commercially available with specifications as follow: assay, 99.9% min.; insolubles, 0.01%; chloride (Cl), 0.01% max.; phosphate, 0.02% max.; iron, 0.005% max. Two GFS standards are available, nos. 14 and 15.

Cerium(IV) can be employed in most titrations where permanganate is used, for example in the determination of iron, ferrocyanide, arsenic, antimony, chromium, oxalates, peroxides, etc. The formal potential of the Ce(IV)/Ce(III) couple depends on the nature and concentration of the acid employed (necessary to prevent precipitation of cerium oxides). In 1 M solutions of acid the formal potentials are 1.28 V for HCl, 1.44 V for H_2SO_4, 1.61 V for HNO_3, and 1.70 V for $HClO_4$. Ceric ammonium nitrate is used infrequently as a titrant, but it is commonly used to prepare standard solutions of cerium(IV) sulfate or perchlorate which are very satisfactory titrants.

To prepare 0.1000 N cerium(IV) sulfate in 1 M sulfuric acid, place 54.83 g of primary standard grade ceric ammonium nitrate (dried at 85 °C for 4 hours) in a 1-l beaker and add 56 ml of 95% sulfuric acid, stir the mixture for 2 minutes, then add 100 ml of water gradually over a period of 5 minutes with stirring (the heat of dilution provides the high temperature necessary to convert the nitrate to the sulfate). Add four more 100-ml portions of water, stirring for 2 minutes after each portion. When the solid is completely dissolved, dilute to exactly one liter in a volumetric flask. Standardization is unnecessary and the solution can be stored in glass without change in normality for at least one year.

Iodine

I_2 F.W. 253.80 (E.W. = 126.90)

Iodine can be obtained in a very pure state by sublimation after mixing it intimately with potassium iodide and lime. The commercially available reagent grade material is a sublimed product that meets the following requirements: form, sublimed crystals; not more than 0.010% nonvolatile matter; not more than 0.005% chlorine and bromine (as Cl). If protected from organic matter and dust the purity of the sublimed product remains that of a primary standard (in excess of 99.9%). It is best stored in an ungreased desiccator and dried over calcium chloride or magnesium perchlorate. Drying in an oven should never be attempted, because iodine is volatile and corrosive.

The following are among the more common substances that can be titrated successfully with iodine using starch as the indicator: arsenic(III), antimony(III), ferrocyanide, mercaptans, phosphite, sulfide, sulfite, and thiosulfate. Proper adjustment of pH is necessary in each case to favor completeness and/or rate of reaction. Titrations involving very alkaline solutions are impractical because iodine reacts with hydroxide ion to form iodide and hypoiodite (which rapidly transforms to iodate and iodide).

To prepare an accurate standard solution of iodine with a normality of the order of 0.1 N the following procedure is recommended: Into a large glass-stoppered weighing bottle, put approximately 40 g of potassium iodide (iodate free) and dissolve in 10 ml of water. Allow the bottle and contents to stand and come to room temperature; then stopper the bottle and weigh accurately. As quickly as possible and without splashing, introduce about 12.7 g of pure iodine (previously weighed on a rough balance). Restopper the bottle and reweigh accurately. Transfer the solution rapidly and quantitatively into a liter volumetric flask; then fill to the mark with distilled water. Shake until the solution is uniform and transfer to a glass-stoppered amber glass bottle. Store the solution in a cool, dark place. The addition of excess potassium iodide provides two advantages: increased solubility and decreased volatility of the iodine. A disadvantage is that iodide can be oxidized by oxygen, catalyzed by acid and sunlight. Hence the iodine solution should not be used for titrations involving very acidic solutions. Furthermore, to avoid volatility losses, iodine solutions should not be exposed unduly and kept in closed containers (preferably in alkali-resistant glass). The normality should be redetermined periodically using arsenious oxide as primary standard.

Potassium Iodate

KIO_3 F.W. 214.00 (E.W. = 35.67, based on reduction to iodide)

Except for its low equivalent weight, potassium iodate is an excellent primary standard. It is available commercially in pure form, easily purified by crystallization from water, and non-hygroscopic. To assure that it is properly dried and freed of occluded water the crystals should be crushed and heated at 150-180 °C for an hour. Reagent grade potassium iodate should meet the following requirements: 0.005% or less insoluble matter, pH 5.0 to 8.0 for a 5% solution at 25 °C, 0.01% or less chloride and bromide (as Cl), 0.001% or less iodide, 0.005% or less nitrogen compounds (as N), 0.005% or less sulfate, 0.0005% or less heavy metals (as Pb), 0.001% or less iron, and not more than 0.0005% sodium. If the reagent grade material has a purity of at least 99.9% it is a suitable standard. GFS Reagent ACS is catalog no. 79.

When used as a standard oxidant, potassium iodate is commonly dissolved and quantitatively converted to iodine (as triiodide complex) by treatment with potassium iodide and a slight excess of acid as per the following reaction:

$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O$$

By this procedure a standard solution of potassium iodate can be used to generate a standard solution of iodine freshly as needed, or it can be used directly as a titrant to generate iodine in situ to react with the sought-for reductant, for example sodium bisulfite, sodium thiosulfate, ascorbic acid, etc. Potassium iodate can also be used as a titrant to determine iodide, iodine, thiocyanate, and a variety of other reducing agents if the titration is carried out in 3 to 9 M hydrochloric acid (25).

To prepare a 0.1000 N solution, dissolve 3.567 g of pure KIO_3 (dried at 180 °C for one hour) and dilute to exactly one liter with distilled water. The solution is stable for long periods and need not be standardized unless evaporative loss is suspected.

Potassium Bromate

$KBrO_3$ F.W. 167.00 (E.W. = 27.83, based on reduction to bromide)

Reagent grade potassium bromate that meets ACS specifications (GFS no. 555) is suitable as a standard. The specifications are as follows: assay, 99.8%; 0.005% or less insoluble matter, pH 5.0 to 9.0 for a 5% solution at 25 °C, 0.05% or less bromide, 0.001% or less nitrogen compounds (as N), 0.005% or less sulfate, 0.0005% or less heavy metals (as Pb), 0.002% or less iron, and not more than 0.01% sodium

The assay procedure is as follows. Dry a powdered sample to constant weight at 150 °C. Weigh accurately about 1 g, dissolve in water, and dilute to 250 ml in a volumetric flask. To a 25-ml aliquot of the solution add 3 g of KI and 3 ml of hydrochloric acid. Allow to stand 5 min. and titrate the liberated iodine with a 0.1 N standard solution of sodium thiosulfate, adding starch indicator solution near the end point. Correct for a blank test. One ml of 0.1000 N $Na_2S_2O_3$ corresponds to 0.002783 g of $KBrO_3$.

Primary standard potassium bromate can be used to standardize sodium thiosulfate solutions (following the same procedure as above except for use of $KBrO_3$ of known purity) and solutions of certain other reductants that react quantitatively with iodine. A standard solution of $KBrO_3$ can be used directly to titrate a variety of reducing agents, including arsenic(III), antimony(III), iron(II), sulfides, and mercaptans. Bromide ion is the reduction product of the bromate. At the end point in these titrations bromide is oxidized to bromine which is readily detectable by its color or with a suitable indicator. Various organic compounds, phenols for example, can also be determined by bromination using a standard solution of potassium bromate to generate the bromine. Excess bromine is generated and then back-titrated (after adding excess potassium iodide) with a standard solution of sodium thiosulfate.

Other Oxidimetric Standards

Potassium hydrogen iodate, described in Chapter II as a primary standard acid, is a very satisfactory standard and can be used in place of potassium iodate. Potassium ferrocyanide, $K_3Fe(CN)_6$, in alkaline solution has found limited application in the determination of reducing sugars (26). Ammonium vanadate, recrystallized and dried, has been recommended as a primary standard (27).

Primary Standard Reductants

Arsenic(III) Oxide

(Arsenious oxide, Arsenic trioxide, Arsenious acid anhydride)
As_2O_3 F.W. 197.84 (E.W. = 49.46, based on oxidation to As(V))

Readily available in a high degree of purity (GFS catalog no. 4), arsenic(III) oxide is an excellent primary standard. When purification is necessary it is ordinarily accomplished by crystallization from 20% hydrochloric acid followed by repeated crystallization from water until the supernatant is no longer acidic to methyl red indicator. Drying to constant weight is best done in a desiccator over concentrated sulfuric acid or anhydrous magnesium perchlorate. It is unsafe to heat arsenic(III) oxide much above 125 °C, as it tends to sublime and the vapor is easily ingested and extremely poisonous. Care and cleanliness is always advisable in handling arsenic(III) oxide because of its great toxicity. Fortunately, it is not hygroscopic, so it can be weighed and handled in the open without risk of it absorbing appreciable moisture.

Arsenic(III) oxide is useful for standardizing solutions of such oxidants as permanganate, cerate(IV), iodine, and bromine. It may also be employed to determine these and other oxidants, most commonly by adding a known quantity of As_2O_3 and back-titrating the excess arsenic(III) with standard iodine or permanganate solution. It is exceedingly slow to dissolve in water, so arsenious oxide is usually dissolved in sodium hydroxide and then its solution is neutralized.

To prepare 0.1000 N arsenic(III) solution, weigh out 4.946 g of pure As_2O_3 (dried over $Mg(ClO_4)_2$ in a desiccator) and dissolve in 60 ml of 1 M NaOH. Neutralize with 60 ml of 1 M HCl and dilute to exactly one liter with distilled water. This solution, if neutral or only slightly acidic, can be stored for months without change in its normality. Alkaline or strongly acidic solutions, however, tend to be more easily oxidized (to arsenic(V)) by atmospheric oxygen and should not be stored.

Sodium Oxalate

$Na_2C_2O_4$ F.W. 134.00 (E.W. = 67.00, based on oxidation to CO_2)

Primary standard grade sodium oxalate is available commercially (GFS no. 90). The National Bureau of Standards can provide a certified sample of effective purity 99.95%. Purification is generally achieved by several crystallizations from water. Solubility in water is about 34 g/l at 20 and 62 g/l at 100 °C. The anhydrous material is obtained by pulverizing the crystals and heating at 240-250 °C for several hours; at lower temperatures, not all of the occluded water is removed. On exposure to air of 70% relative humidity the anhydrous solid picks up approximately 0.01% water, but this is primarily surface moisture and can be removed by drying at 105 °C. The solid is very stable but solutions of sodium oxalate should not be stored in glass that may contain calcium which can react with it and precipitate calcium oxalate.

The major use of sodium oxalate in titrimetry is for standardizing solutions of permanganate, cerium(IV) and vanadium(V). It has been recommended also as a primary standard for standardizing solutions of strong acids, since it can be thermally decomposed to pure sodium carbonate.

Standard solutions of sodium oxalate should be kept in the dark, preferrably in polyethylene bottles, and not retained longer than one year. Otherwise, loss in normality due to decomposition ($H_2O + C_2O_4^{=} \rightarrow CO_2 + CO + 2OH^-$), catalyzed by light, becomes appreciable.

Iron

Fe F.W. 55.845

According to ACS specifications reagent grade iron wire or pieces should have a purity of not less than 99.90 or more than 100.00%, based upon titration of the ferrous sulfate produced on dissolving the iron in oxygen-free, dilute sulfuric acid. Available commercially, iron of this purity is most commonly prepared by electrolysis followed by ignition in moist hydrogen. It may also be prepared from iron carbonyl (28). Electrolytic iron is GFS catalog no. 226.

Pure iron is a useful primary standard for standardizing solutions of permanganate or cerium(IV), especially when these titrants are to be employed to determine iron in ores or metallurgical samples.

It is not necessary to dry the iron prior to use, but it should be stored dry in a closed vessel to protect it from rusting.

Other Reductimetric Standards

Oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$, F.W. 126.07, E.W. 63.03) can be used to standardize solutions of permanganate (29) as well as strong alkalies (30). In place of pure iron, either Mohr's salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$-(F.W. 392.14), (31) or potassium ferrocyanide trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$ (F.W. 422.41) (32) can be used to standardize permanganate or cerium(IV) solutions; however these hydrates are more properly classified as secondary rather than primary standards. Ferrous ethylenediamine sulfate, Fe-$C_2H_4(NH_3)_2(SO_4)_2$ (F.W. 382.15), has been recommended as a standard for permanganate, dichromate and cerium(IV) solutions (33). Barium thiosulfate monohydrate, $BaS_2O_3 \cdot H_2O$ (F.W. 267.51), is reported to be an excellent iodometric standard (34).

Standard Solutions

General details concerning accurate preparation and use of standard solutions are summarized in Chapter II under the subheading Standard Solutions.

Specific information for some commonly used redox titrants is given in the following subsections.

Cerium(IV) sulfate

Standard solutions can be prepared directly using primary standard grade ammonium hexanitratocerate(IV), as described above. Alternatively, they can be prepared by dissolving either ceric sulfate, ceric ammonium sulfate or ceric hydroxide in sulfuric acid and then standardized with arsenic(III) oxide, sodium oxalate or electrolytic iron.

To prepare approximately 0.1 $\underline{N}$ cerium(IV) solution (0.5 $\underline{M}$ in H_2SO_4), slowly add 30 ml of concentrated sulfuric acid to 63 g of ceric ammonium sulfate (or 53 g of ceric sulfate) stir to form a smooth paste, then slowly and carefully add water in small amounts with stirring until solution is complete (300-500 ml), cool to room temperature, filter the solution if turbid, and dilute to one liter. If the solution must be filtered, do not use paper or similar material as the titer will be affected. Standardize the solution using primary standard As_2O_3, a trace of osmium tetroxide as catalyst and ferroin as indicator.

On storage, ceric phosphate may precipitate from ceric solutions if traces of phosphate are present in the starting materials. When left to stand for 2 weeks or longer and then filtered to remove ceric phosphate before standardizing, ceric sulfate solutions (0.1-1.0 $\underline{M}$ in H_2SO_4) are stable for years at 25 °C.

Potassium permanganate

No primary standard grade permanganate is available, so a solution of the approximate desired concentration is prepared using potassium permanganate and standardized against a suitable primary standard reductant. Care to remove manganese dioxide, which catalyzes autodecomposition of permanganate and which is slowly produced when neutral permanganate solutions are contacted with organic debris, is necessary to assure a long storage life. Regular standardizations are recommended.

To prepare 0.1 $\underline{N}$ $KMnO_4$ dissolve 3.2 g of reagent grade potassium permanganate (F.W. 158.03) in one liter of water, heat the solution just below boiling for one hour, filter through a sintered-glass filter crucible or glass-fibre mat, and transfer the filtrate to a clean (grease-free) glass-stoppered bottle. Protect the solution from sunlight, dust, reducing vapors, and evaporation loss. If manganese dioxide precipitates on long standing, refilter and restandardize the solution.

Depending on its end use, the permanganate solution should be standardized with primary standard arsenious acid, sodium oxalate, or electrolytic iron. The permanganate solution is self indicating as a titrant so long as its concentration is 0.1 $\underline{N}$ or greater. A suitable indicator, dependent on the reductant titrated, is necessary for 0.01 $\underline{N}$ or less concentrated permanganate solutions.

Sodium thiosulfate

A standard solution of a soluble thiosulfate salt serves as an excellent titrant for the determination of iodine, as well as for any oxidant that is caused first to react with an excess of potassium iodide to quantitatively yield iodine. Although barium thiosulfate, among others, has been advocated as a primary standard for this purpose, sodium thiosulfate is most commonly employed, even though it is neither a primary nor secondary standard substance.

To prepare approximately 0.1 N $Na_2S_2O_3$, dissolve 25 g of sodium thiosulfate pentahydrate (F.W. 248.17) together with 0.1 g of sodium carbonate in one liter of freshly boiled, cooled water. Allow the solution to stand for a day, and then standardize it against primary standard grade potassium iodate, potassium dichromate, or iodine, adding starch indicator near the end to detect the equivalence point.

Thiosulfate solutions decompose slowly with time, due primarily to the action of certain micro-organisms which, although easily destroyed, are widely distributed and difficult to exclude from solutions exposed to air. Bacterial action is slower between pH 9 and 10, so addition of sodium carbonate is helpful. Air oxidation also contributes to the gradual decomposition. Thus, thiosulfate solutions should be standardized just prior to use or checked periodically (every few days) if exposure to air is prolonged. Once turbidity develops or sulfur deposits appear, the solution should be discarded. The stock bottle should not be used again until it is cleaned and sterilized (hot chromic acid is suitable).

Iron(II) sulfate

Titrimetric determination of certain oxidants, notably permanganate, cerium(IV), dichromate, and vanadium(V), can be accomplished effectively using ferrous sulfate as titrant. Choice of indicator depends on the oxidant to be determined and the acidity of the titrate solution.

Either ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt), or ferrous ethylenediammonium sulfate, $FeC_2H_4(NH_3)_2 \cdot (SO_4)_2 \cdot 4H_2O$ (Oesper's salt), is generally used in preference to ferrous sulfate when standard solutions of iron(II) are to be prepared. These compounds are available in high purity and, once assayed for exact purity, they serve as excellent secondary standards for preparation of standard solutions directly by dissolving known weights in measured volumes of dilute sulfuric acid.

To prepare 0.1000 N iron(II) sulfate, dissolve 3.922 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (F.W. 392.14) (99.9-100.1% purity by assay) (do not dry) or 3.822 g of Oesper's salt (F.W. 382.16) (assay 99.9% min.) (do not dry) in 0.5 M sulfuric acid and dilute (with the same acid) to a volume of exactly one liter. The normality of this solution will decrease very slowly on exposure to air due to oxidation of ferrous to ferric ions by oxygen. In neutral or concentrated solutions of strong acids, air oxidation is more rapid than in dilute acid. If allowed to stand more than a day, the ferrous sulfate solution should be standardized against a standard solution of the same oxidant that is to be determined in subsequent titrations with the ferrous sulfate solution.

Chapter IV. STANDARDS FOR CHELOMETRIC AND PRECIPITATION TITRATIONS

Chelometric titrations are performed either to determine metal ion concentrations or to determine chelon concentrations. Determinations of calcium, magnesium, and water hardness with EDTA are the most common titrations of this kind. Precipitation titrations involve metal ions also, either their determination or their utilization as titrant species. The most common, certainly the most reliable, titrations of this kind are those that employ a standard solution of silver nitrate for determination of halides (chloride, bromide, or iodide) or pseudo-halides (cyanide, azide, or thiocyanate). Titrants and suitable primary and secondary standards for EDTA as well as argentimetric titrations are described below. Other standards are mentioned only briefly in separate paragraphs below.

Disodium Dihydrogen Ethylenediaminetetraacetate Dihydrate

(EDTA, disodium salt, dihydrate)
$HOCOCH_2(NaOCOCH_2)NCH_2CH_2N(CH_2COONa)CH_2COOH \cdot 2H_2O$
F.W. 372.26

Disodium EDTA is available commercially in a primary standard grade which is 99.9 to 100.1% in assay when used as received (GFS no. 365). Because of the difficulty in drying the product to control the water content, it is not an ideal primary standard. The analyzed reagent grade material is suitable for the direct preparation of standard solutions of sufficient accuracy (± 0.2% relative error) for many routine determinations. For greater accuracy the EDTA solution should be standardized versus a suitable primary standard.

To prepare 0.1000 M EDTA, dissolve 37.22 g of the disodium ethylenediaminetetraacetate dihydrate (dried at 80 °C in a relative humidity of 50% for several days, not dried if an assay indicates a purity of 100.0% or as received if primary standard is purchased) in about 800 ml of distilled (or de-ionized) water and dilute exactly to one liter with the same water. Store the solution in a tightly closed polyethylene bottle, where it will retain its effective concentration indefinitely.

If the purity of the EDTA salt or the molarity of the solution is in doubt, standardize the solution using either primary standard calcium carbonate and calcein as indicator (35) or primary standard magnesium iodate tetrahydrate and calmagite or Eriochrome Black-T as indicator (36).

Silver Nitrate

$AgNO_3$ F.W. 169.89

Recrystallization from water containing a small amount of nitric acid is an effective means of removing trace impurities from silver nitrate. If not for the crucial treatment required to remove traces of occluded water, silver nitrate would qualify as a primary standard. Commercially available reagent grade material is commonly at least 99.7% pure; after drying at

110 °C, it can be used to prepare standard solutions by direct weighing if relative errors of a few ppt are acceptable. For greater accuracy, the silver nitrate should be dried first at 110 °C and then heated (melted) for 15 minutes at 220-250 °C (in the dark and very clean surroundings) to expel occluded water. Alternatively, the exact concentration of the silver nitrate solution can be determined by standardization against primary standard sodium chloride.

To prepare 0.1000 $\underline{M}$ silver nitrate, dissolve 16.99 g of pure silver nitrate (pulverized and dried at 110 °C) in distilled water, dilute to a volume of exactly one liter, and store the solution in a clear bottle protected from sunlight, coated with red lacquer or covered with black paper.

To check the normality, in case of doubt as to purity or solution stability, use sodium chloride as primary standard and either the Mohr method (potassium chromate as indicator) or the Fajans method (dichlorofluorescein as indicator) to standardize the silver nitrate solution.

Calcium Carbonate

$CaCO_3$ F.W. 100.09

As a chelometric standard, calcium carbonate must assay not less than 99.95 and no more than 100.05% $CaCO_3$. Samples of this purity are readily available commercially and need only to be dried at 100 °C prior to weighing out portions for use in standardizing solutions of EDTA or other chelons (GFS catalog no. 337).

To prepare one liter of 0.01000 $\underline{M}$ calcium chloride (for use in standardizing 0.01 $\underline{M}$ EDTA and other chelons) transfer 1.001 g of calcium carbonate (dried at 100 °C) into a 1-liter volumetric flask, add 6 ml of concentrated hydrochloric acid to dissolve the carbonate, and dilute with distilled water to exactly one liter. After thorough mixing, transfer the solution to a clean, dry bottle for storage. Solution stability on storage is excellent and standardization is unecessary.

Magnesium Iodate Tetrahydrate

$Mg(IO_3)_2 \cdot 4H_2O$ F.W. 446.20

As found by Lindstrom and Stephens (36) this compound has all the desirable properties of a primary standard, even a high formula weight to minimize relative errors in weighing. It is easily prepared from magnesium carbonate and a slight excess of iodic acid, and it can be readily purified by crystallization from water at 55 °C (below 13.3 °C a decahydrate forms and above 57.5 °C the anhydrous salt forms). The tetrahydrate can be dried in air, where it is stable even at a relative humidity of 98%. It can even be stored over magnesium perchlorate, a strong desiccating agent, without loss of water. The surprisingly stable tetrahydrate is readily soluble and ideally suited for standardizing EDTA solutions, even providing the magnesium required by Eriochrome Black-T or Calmagite to respond properly as indicators in the titration. The GFS catalog no. is 348.

To prepare 0.01000 $\underline{M}$ magnesium iodate, dissolve 4.462 g of $Mg(IO_3)_2 \cdot 4H_2O$ (air dried) in distilled water and dilute to a volume of exactly one liter. The solution may be stored indefinitely without change in a tightly closed boro-silicate glass or polyethylene bottle. Standardization is unnecessary, even after prolonged storage.

Sodium Chloride

NaCl F.W. 58.443

Once it has been properly dried, reagent grade sodium chloride is a primary standard substance. According to ACS requirements, reagent grade sodium chloride should have no more than 0.002% iodide and no more than about 0.01% bromide, hence errors due to interference from these halides in the titration with silver nitrate should be negligible (less than 0.1 part per thousand). For most purposes, reagent grade sodium chloride can be sufficiently dried by first pulverizing it to a powder and then heating it in an oven at 150 °C to constant weight (about 1 hour). Heating the powdered material to constant weight in an electric furnace at 500-600 °C can be employed if a completely dried sample is desired for highest accuracy. The dried salt is not hygroscopic and can be stored without change in a glass-stoppered bottle. Aqueous solutions are also stable indefinitely.

To prepare 0.1000 $\underline{M}$ sodium chloride, transfer an accurately weighed sample (5.844 g) of powdered reagent-grade sodium chloride (dried one hour at 150 °C) to a 1-liter volumetric flask, add distilled water to dissolve the salt, dilute to exactly one liter, mix thoroughly, and transfer the solution to a clean, dry bottle for storage. Standardization is unnecessary, even after prolonged storage.

Other Chelometric Standards

Various metal ion solutions can be used to standardize solutions of chelons (e.g., EDTA) and for back-titration procedures. These are prepared by dissolving an accurately weighed sample of pure metal or salt and dilution to a known accurate volume. Some of the more commonly used substances are the following: bismuth, copper (electrolytic), iron, ferrous ammonium sulfate hexahydrate, mercury, nickel, lead(II) oxide, and zinc.

Other Precipitimetric Standards

Potassium sulfate, pulverized and dried at 800 °C, is a practical standard for standardizing barium chloride solutions prepared for titrimetric determination of sulfur as sulfate.

Metallic silver of high purity, available commercially, is suitable for preparing standard solutions of silver nitrate. Similarly, zinc and mercury are commercially available in high purity for use in preparing standard solutions of their metal ions. Standard solutions of zinc may be used to titrate ferrocyanide ions, and mercury(II) to titrate halides and thiosulfate ions.

Chapter V. STANDARDS FOR MICROANALYSIS AND INSTRUMENT CALIBRATION

Although instrumental measurements frequently can be made both rapidly and precisely, their accuracy is limited primarily by the reliability of the instrument calibration. The signal or response of any particular instrument to a given input or sample must be calibrated using a standard input or known sample if the instrument is to yield meaningful results. Also, some instruments require more frequent calibration than others. Thus standards that are both reliable and readily available are essential for instrumental methods of analysis. In the sections that follow, only some of the more commonly used standard samples for calibrating the more frequently employed instruments are described. For information concerning calibration standards for more specialized instruments and applications, one can refer to publications available from the National Bureau of Standards (37).

Organic Reference Standards for Elemental Analysis

Organic compounds of reliably known elemental composition are frequently used for method evaluation and to check on the accuracy of carbon, hydrogen, nitrogen, sulfur and halogen determinations carried out by classical gravimetric or volumetric procedures. With the advent of automated elemental analyzers (based on thermal conductivity detection of separated combustion products of weighed samples), organic reference standards assumed an even more important role, because these instruments must be properly calibrated to enable a measured response to be equated to the amount of element detected. The following substances are reliable reference standards for most purposes if they are reagent grade quality (meet ACS requirements) and properly dried. For microanalysis they should be pulverized (before drying) to assure homogeneity, which becomes more crucial as smaller sample sizes (1-10 mg) are taken.

Acetanilide

C_8H_9NO F.W. 135.16

Elemental composition: 71.09% C, 6.71% H, 10.36% N, and 11.84% O.
Dry over anhydrous magnesium perchlorate in an evacuated desiccator.
Melting point 113-115 °C, volatile at 85 °C

Sulfanilic Acid

$C_6H_7NO_3S$ F.W. 173.84

Elemental composition: 41.61% C, 4.07% H, 8.09% N, 18.51% S, and 27.72% O.
Dry at 110 °C in an oven. Decomposes without melting above 280 °C.

m-Chlorobenzoic Acid

$C_7H_5ClO_2$ F.W. 156.67

Elemental composition: 53.69% C, 3.22% H, 22.65% Cl, and 20.44% O.
Dry at 110 °C in an oven. Melting point 158 °C.

Standards for Trace Element Determinations

Trace element determinations based on such commonly used techniques as atomic absorption, flame emission, ion-selective potentiometry, polarography, anodic stripping voltammetry, and ion-chromatography involve the use of standards to calibrate the instruments. Invariably, the calibration standards for these are solutions that are accurately prepared from primary standards or standardized against a primary standard. Some of the more commonly used standards for these purposes are included in the list that follows. Not included are standards of the special type required when matrix effects must be taken into consideration, for example in analysis of solid mixtures and alloys by X-ray emission spectrometry. Some standards of this type are available as SRM samples from the National Bureau of Standards.

Metals

Aluminum, copper, iron (electrolytic), lead, mercury, tin, and zinc are suitable standards if they are reagent grade (meet ACS requirements).

Salts

Some reagent grade salts are suitable working standards for preparing standard calibration solutions, particularly when the inherent relative error of the instrumental measurement is of the order 1-2%. For greater accuracy, primary standard substances are available for certain elements. These include all of the standard substances described in Chapters II-IV.

Solutions

Standard solutions are commercially available. These afford a convenient and inexpensive means of calibrating instruments that are only operated occasionally or where laboratory facilities or personnel preclude their preparation and standardization. GFS Chemicals, for example, markets standard solutions of the following elements and ions: Aluminum, ammonium, arsenic, barium, boron, bromide, cadmium, calcium, cerium, chloride, chromium, cobalt, copper, iron, lanthanum, lead, lithium, magnesium, manganese, mercury, nickel, nitrate, perchlorate, phosphate, potassium, silver, sodium, strontium, sulfate, tin, vanadium and zinc. All of these solutions contain 1.000 mg/ml of the element in question. In addition, solutions containing 2, 5, and 10 μg/ml are available for copper, and 1 and 10 μg/ml for iron.

Miscellaneous Calibration Standards

Various standard buffer solutions are available for calibrating pH meters. The most commonly used are those of pH (at 25 °C) 4.01, 6.86, 7.41, 7.70, 9.18 and 10.01. They may be prepared using primary standard grade, NBS standard reference materials (for highest accuracy), or ACS reagent grade compounds. Some compositions are as follows: for pH 4.01, 0.050 $\underline{M}$ potassium acid phthalate; for pH 6.86, an equimolar (0.025 $\underline{M}$) solution of KH_2PO_4 and Na_2HPO_4; for pH 7.41, a solution 0.0087 $\underline{M}$ in KH_2PO_4 and 0.0304 $\underline{M}$ in Na_2HPO_4; for pH 9.18, 0.01 $\underline{M}$ $Na_2B_4O_7$; and for pH 10.01, an equimolar (0.025 $\underline{M}$) solution of $NaHCO_3$ and Na_2CO_3.

Although calorimeters are best calibrated by electrical means, chemical substances are occasionally used as calibration standards to check the accuracy of calorimetric measurements. Two such standards are benzoic acid and tris (hydroxymethyl)aminomethane, and both are available as primary standard grade materials (see Chapter II). The former is most useful as a combustion calorimetric standard ($\Delta H = -26.434$ kJ/g); the latter serves well in calibrating calorimeters for use in measuring heats of solutions or heats of reactions in solutions.

The International Temperature Scale is based on certain fixed points each involving two different states of a single pure substance in thermal equilibrium. For example, ice in thermal equilibrium with air-saturated water provides the temperature point 0.000 °C. Other points include that defined by liquid water and steam at one atmosphere (100.00 °C), liquid and gaseous sulfur (444.60 °C), solid and liquid silver (960.8 °C), solid and liquid gold (1063 °C). Some useful secondary calibration standards, based on freezing points, are benzoic acid (122.36 °C), tin (231.85 °C), lead (327.5 °C), and zinc (419.6 °C). Thermometric standards based on boiling points are also available (38) but not as convenient in use as those based on freezing points.

APPENDIX

TABLE A-1. Temperature Corrections for Volumes and Normalities

Volumetric flasks, pipets and burets are normally calibrated at 20 °C. Their volumes and those of any solution contained in or delivered from them will naturally change with temperature. For exact work therefore one should either make all measurements at 20 °C or calibrate volumetric glass-ware and solutions at the temperature prevailing during the measurements. For most purposes it is possible to avoid extra calibrations by employing theoretical corrections using known coefficients of thermal expansion for glass as well as the particular solution to correct a known volume accurate at one temperature to that at another temperature. The following compilation of data (39) provides the means for making such temperature corrections, assuming 0.000027 as the expansion coefficient for the glassware.

Temp., °C	Water, 0.01 N Solns., or 0.1 N HCl	0.1 N Solns.	0.5 N HCl	1.0 N HCl	0.5 N NaOH	1.0 N NaOH
5	+1.5	+1.7	+1.9	+2.3	+2.35	+3.6
6	1.5	1.65	1.85	2.2	2.25	3.4
7	1.4	1.6	1.8	2.15	2.2	3.2
8	1.4	1.55	1.75	2.1	2.15	3.0
9	1.4	1.5	1.7	2.0	2.05	2.7
10	1.3	1.45	1.6	1.9	1.95	2.5
11	1.2	1.35	1.5	1.8	1.8	2.3
12	1.1	1.3	1.4	1.6	1.7	2.0
13	1.0	1.1	1.2	1.4	1.5	1.8
14	0.9	1.0	1.1	1.2	1.3	1.6
15	0.8	0.9	0.9	1.0	1.1	1.3
16	0.6	0.7	0.8	0.8	0.9	1.1
17	0.5	0.6	0.6	0.6	0.7	0.8
18	0.3	0.4	0.4	0.4	0.5	0.6
19	0.2	0.2	0.2	0.2	0.2	0.3
20	0.0	0.0	0.0	0.0	0.0	0.0
21	−0.2	−0.2	−0.2	−0.2	−0.2	−0.3
22	0.4	0.4	0.4	0.5	0.5	0.6
23	0.6	0.6	0.7	0.7	0.8	0.9
24	0.8	0.9	0.9	1.0	1.0	1.2
25	1.0	1.1	1.1	1.2	1.3	1.5
26	1.3	1.4	1.4	1.4	1.5	1.8
27	1.5	1.7	1.7	1.7	1.8	2.1
28	1.8	2.0	2.0	2.0	2.1	2.4
29	2.1	2.3	2.3	2.3	2.4	2.8
30	2.3	2.5	2.5	2.6	2.8	3.2

Illustrations: If a solution of Hydrochloric acid which is 0.5000 $\underline{N}$ at 20 °C is to be employed at 25 °C, what is its normality?

$\underline{N}$ at 25 °C = $\underline{N}$ at 20 °C $\left(\frac{1000}{1000 - n}\right) = 0.5000 \left(\frac{1000}{1000 - (-1.1)}\right) = 0.4994$

If 25.00 ml of a 0.1 $\underline{N}$ solution at 26 °C is delivered by pipet, what volume would the solution have at 20 °C?

V at 20 °C = V at 26 °C $\left(\frac{1000}{1000 + n}\right) = 25.00 \left(\frac{1000}{1000 + 1.4}\right) = 24.96$

Table A-2. APPROXIMATE DENSITIES and MOLARITIES of CONCENTRATED ACIDS AND AMMONIA

	wt. %	Density, g/ml	Molarity
Acetic Acid	99.5	1.05	17.4
Ammonium hydroxide	27 (NH_3)	0.90	14.3
Hydrochloric acid	37	1.18	12.0
Hydrofluoric acid	48	1.15	27.6
Nitric acid	70	1.41	15.7
Perchloric acid	70	1.66	11.6
Phosphoric acid	85	1.69	14.7
Sulfuric acid	95.5	1.83	17.8

Table A-3. DENSITIES OF ACIDS AND AMMONIA AT 20 °C

wt. %	$HClO_4$	HCl	HNO_3	H_3PO_4	H_2SO_4	NH_3
5	1.027	1.023	1.026	1.025	1.032	0.977
10	1.058	1.047	1.054	1.053	1.066	0.958
15	1.091	1.073	1.084	1.082	1.102	0.940
20	1.125	1.098	1.115	1.113	1.139	0.923
25	1.163	1.124	1.147	1.146	1.178	0.907
30	1.204	1.149	1.180	1.181	1.219	0.892
35	1.247	1.174	1.214	1.216	1.260	
40	1.294	1.198	1.246	1.254	1.303	
45	1.347		1.278	1.293	1.348	
50	1.405		1.310	1.335	1.395	
55	1.467		1.339	1.379	1.445	
60	1.533		1.367	1.426	1.498	
65	1.603		1.391	1.475	1.553	
70	1.672		1.413	1.526	1.611	
75			1.434	1.579	1.669	
80			1.452	1.633	1.727	
85			1.469	1.689	1.779	
90			1.483	1.746	1.814	
95			1.493	1.807	1.834	
100			1.513	1.870	1.831	

PRIMARY and SECONDARY STANDARDS SUPPLIED BY GFS CHEMICALS

Acetanilide
Arsenic Trioxide
Calcium Carbonate
Ceric Ammonium Nitrate
Cobalt Sulfate
Diphenylguanidine
Disodium EDTA
Ferrous Ethylenediammonium Sulfate
Iron
Magnesium Iodate Tetrahydrate
Perchloric Acid
Potassium Acid Phthalate
Potassium Bi-Iodate
Potassium Dichromate
Sodium Oxalate
Sulfamic Acid
Trishydroxymethylaminomethane

STANDARD SOLUTIONS

Volumetric

Ceric Sulfate
EDTA
Hydrochloric Acid
Perchloric Acid
Potassium Dichromate
Silver Nitrate
Sodium Thiosulfate
TPTZ Ferrous Sulfate

Elemental and Ion Standards

Aluminum
Ammonium
Arsenic
Barium
Boron
Bromide
Cadmium
Calcium
Cerium
Chloride
Chromium
Cobalt
Copper
Iron
Lanthanum
Lead
Lithium
Magnesium
Maganese
Mercury
Nickel
Nitrate
Perchlorate
Phosphate
Potassium
Silver
Sodium
Strontium
Sulfate
Tin
Vanadium
Zinc

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